PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

#10/Declaration
Amd
9/25/03

In re Application of)
)
KLEINBERG, ROBERT L.)
)
Application N°: 09/133,234) Group Art Unit: 2862
)
Filed: herewith) Examiner: D. Vargas
)
Title: MAGNETIC RESONANCE METHOD FOR CHARACTERIZING FLUID SAMPLES WITHDRAWN FROM SUBSURFACE EARTH FORMATIONS) Docket N°: 60.1323/1324

DECLARATION UNDER 37 C.F.R. §1.131(a)

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

I, Robert L. Kleinberg, do hereby declare and state:

1. I am the inventor of the claims of the U.S. Patent Application Serial No. 09/133,234 entitled "Magnetic Resonance Method for Characterizing Fluid Samples Withdrawn from Subsurface Earth Formations" filed on 13 August 1998 and of the claims as amended in the Preliminary Amendment submitted herewith (hereinafter referred to as the "Application").

2. On or about 5 August 1997, I prepared a patent memorandum entitled "Downhole PVT Lab for MDT", submitted herewith as Exhibit A.

3. I signed and dated each page of Exhibit A on 5 August 1997.

4. Two witnesses signed and dated each page of Exhibit A on 5-6 August 1997.

5. Pages 3-9 of Exhibit A describe nuclear magnetic resonance (NMR) and electron spin resonance (ESR) measurements on a fluid in a flow line.

6. Figure 1 on page 7 of Exhibit A illustrates an embodiment of a flow line NMR apparatus and forms the basis for Figure 2 of the Application.

7. Exhibit A was submitted to the Patents Department of Schlumberger-Doll Research in Ridgefield, CT 06877 on or about 18 August 1997. Exhibit B contains the memorandum that accompanied the submission of Exhibit A.

8. On or about 29 August 1997, I prepared a patent memorandum entitled "Flow Line NMR Measurements for MDT", submitted herewith as Exhibit C.

9. I signed and dated Exhibit C on 29 August 1997.

10. Two witnesses signed and dated Exhibit C on 29 August and 5 September 1997.

11. Pages 1-11 of Exhibit C describe additional NMR measurements on a fluid in a flow line.

12. Exhibit C was submitted to the Patents Department of Schlumberger-Doll Research on or about 17 September 1997. Exhibit D contains the memorandum that accompanied the submission of Exhibit C.

13. Pages 3-9 of Exhibit A and pages 1-11 of Exhibit C form the basis for the subject matter of the Application and the claims thereof.

14. On or about 21 October 1997, Exhibits A and C were forwarded by Keith Smith, then Patent Manager of the Schlumberger-Doll Research Patents Department, to Mark Levy, Esq., at Salzman & Levy, Binghamton, NY 13901 with instructions to prepare one or more patent applications. Exhibit E contains the cover letter from Keith Smith to Mark Levy that accompanied Exhibits A and C.

15. On or about 6 January 1998, Mark Levy forwarded to Keith Smith a draft patent application ("Draft") based on at least Exhibit A. The cover letter that accompanied the Draft is Exhibit F.

16. Between about 6 January and about 20 March 1998, I reviewed the Draft and provided comments about the Draft to Keith Smith.

17. On or about 20 March 1998, Keith Smith responded to Mark Levy with the letter contained in Exhibit G.

18. Exhibit G notes that the Draft is believed intended to include both Exhibits A and C.

19. Exhibit G further notes that the Draft "needs considerable re-work".

20. Between about 20 March and 13 August 1998, I worked with Keith Smith on several revisions of a patent application and claims based on Exhibits A and C.

21. All statements made herein of my own knowledge are true, and all statements herein made on information and belief are believed to be true. The statements herein were made with knowledge that willful false statements and the like are punishable by fine or imprisonment or both under 18 U.S.C. §1001, and that such willful false statements may jeopardize the validity of the Application or any patent issuing thereon.

Robert L. Kleinberg
Robert L. Kleinberg

10 May 2001
Date

OIPE JC32
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EXHIBIT A

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SCHLUMBERGER-DOLL RESEARCH
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PATENT MEMORANDUM

Inventor : **R.L. Kleinberg** Date: 5 August 1997

First Disclosures: Presentation to A. Gould and A. Belani, SDR, 23 January 1997;
SDR EMG-006 Program Review, 14 May 1997

Title of Invention: **Downhole PVT Lab for MDT**

1. Introduction

The Schlumberger Modular Formation Dynamics Tester (MDT) can take samples of formation fluids and transport them to the surface. The samples are transferred from sampling bottles to transportation bottles, then sent to PVT (pressure-volume-temperature) labs for analysis of composition and physical properties. Up to six samples can be collected on each trip in the hole. The samples undergo reversible and irreversible changes as a result of the temperature change while being brought uphole, and as a result of the transfer process.

I propose an MDT module which can make some of the most important measurements now being made in PVT labs. The purpose of a Downhole PVT Lab is to provide means of making a partial analysis when the sample is taken, after which the

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sample can be saved for further analysis or discarded to the borehole. In this manner an unlimited number of fluid samples can be analyzed on each trip in the hole. The measurements are made at formation temperature and pressure, after minimum manipulation, thus helping to ensure sample integrity. Transportation and disposal problems are minimized or eliminated.

Conventional PVT labs provide a broad range of measurements and services, and there is no intention of duplicating all those services in the downhole module. SPC Mechanical has commissioned a fluid sampling market report and has organized an MDT Client Advisory Board, from which I have determined that the following measurements would be most valuable to implement in a downhole tool: (1) density, (2) bubble point, (3) viscosity, and (4) composition. Dew point of gas condensates is also easily determined in the same apparatus.

Sample contamination is universally regarded as the most serious problem associated with downhole fluid sampling. First, it is essential that formation fluid, not mud filtrate, is collected in the sample chambers of the tool. Second, even small amounts of mud filtrate contamination can have important effects on the physical properties of the fluid sample. Thus it is important to both detect and quantify mud filtrate in the fluid sample.

The Optical Fluid Analyzer (OFA) can detect contamination in many cases. It is particularly effective when the mud filtrate is aqueous and the flowing formation fluid is pure hydrocarbon, since there is a large contrast between water and oil in the near infrared band. However, it does less well when the filtrate is oil based, or when the formation fluid is a mixture of oil and water. The addition of other flow line measurements can substantially aid contamination identification and quantification.

There are regular reports of competitors' activities in fluid sampling, including recently issued patents, at http://tw.austin.sar.slb.com/competition/sampling/.

2. Overview

The proposed PVT module for the MDT tool has two components, an instrumented flow line, and a pressure-volume expansion (PV) cell.

The instrumented flow line monitors produced fluid for mud filtrate contamination. The physical properties of formation fluid can be determined by making a final measurement when it has been determined that contamination is reduced to a negligible level. Native fluids can also be characterized by measuring their physical properties during mud filtrate clean up, and extrapolating the results to zero contamination level. The present MDT pump out module can be used to draw fluids from the formation, circulate them through the instrumented flow line, and expel this fluid to the borehole, or save them in a sample bottle for further analysis uphole. The instrumented flow line described here can be used in series with the Optical Fluid Analyzer.

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Once it has been determined that contamination has been reduced to a sufficiently low level, fluid can be pumped into the PV cell for further testing. After the cell is filled, it is isolated from the flow line. Then a piston, similar to that used in the present MDT sample chamber, is displaced in small measured increments, and the pressure is measured. This provides basic PV information, such as bubble point. In addition, the PV cell can be instrumented to provide further measurements as a function of pressure.

3. Flow Line Measurements

3.1 Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is a natural component of an MDT fluid analysis module. It can serve two distinct functions: (1) monitoring contamination as fluid draw down proceeds, and (2) measuring material properties of the fluids, when it has been determined that the sample is completely or predominantly formation fluid. Both functions can be performed in the flow line during, or at the conclusion of, draw down. Nuclear magnetic resonance of ^1H (protons) is preferred because of the ubiquity and good NMR characteristics of this nuclear species. However, magnetic resonance of other nuclear and electronic species are useful and can be performed by the same apparatus, as detailed below.

3.1.1 Oil Base Mud Filtrate vs. Formation Oil

There are a number of possible NMR-detectable contrasts between oil base mud (OBM) filtrates and formation oils: (1) viscosity, (2) composition, (3) trace element content (natural or introduced), (4) diffusion coefficient, (5) proton density, and (6) molecular conformation.

Viscosity: Extensive measurements on pure substances and crude oils have found an excellent correlation between fluid viscosity and the NMR relaxation times (T_1 and T_2) [Bloembergen et al "Relaxation Effects in Nuclear Magnetic Resonance Absorption", Physical Review 73, 679-712 (1948); Morriss et al "Hydrocarbon Saturation and Viscosity Estimation from NMR Logging in the Belridge Diatomite", Log Analyst, Mar-Apr 1997, pg 44-59]. For very viscous liquids, the dependence of T_2 on viscosity weakens, and T_1 becomes longer than T_2; however, such liquids are outside the range of operation of the present MDT.

In general, the viscosity of OBM filtrate is different (higher or lower) than that of the formation oil. Thus measurements of NMR relaxation time can distinguish these fluids from one another. Moreover, when OBM filtrate is mixed with formation oil, the viscosity, and therefore relaxation time, of the mixture will be intermediate between the viscosities of the individual components.

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Viscosity of the formation oil, and the level of contamination during draw down, can be quantified by a continuous measurement of NMR T_2, hence viscosity. As draw down continues, the time dependence of viscosity of the oil phase in the flow stream, $\eta(t)$, will vary as

$$\eta(t) = \eta_{mf} + \left[(\eta_n - \eta_{mf}) f(t)\right] \tag{1}$$

where η_{mf} is the viscosity of the mud filtrate under downhole conditions, which can be measured in advance in a laboratory, and η_n is the unknown viscosity of the formation oil. f(t) depends on fluid and formation properties and is therefore unknown. However, f(t) is expected to be subject to the conditions that $f(0) \geq 0$, $df/dt > 0$, $d^2f/dt^2 < 0$ (at least at long time), and $f(\infty) = 1$. Given a sufficiently long acquisition of data, η_n can be estimated from the long-time asymptote of $\eta(t)$, and contamination level at any given time can be estimated.

Composition: Oil base mud filtrates are characterized by a narrow distribution of relaxation times [J.H. Lee, "NMR Relaxation Times of Drilling Fluid Filtrate Mixtures at Elevated Temperatures", Department of Chemical Engineering, Rice University, 1996]. In contrast, crude oils have broad distributions of relaxation times [Morriss et al, "Hydrocarbon Saturation and Viscosity Estimation from NMR Logging in the Belridge Diatomite", Log Analyst, Mar-Apr 1997, pg 44-59]. Thus even if the OBM filtrate and native crude have the same viscosity, NMR T_2 analysis will be able to distinguish them based on the distribution of relaxation times.

In addition, the shape of the T_2 distribution of crude oils may correlate with composition. Thus it may be possible to obtain a crude composition analysis of formation oils from NMR relaxation measurements.

Trace Element Content: Trace elements can be detected in two distinct ways. (1) Paramagnetic ions or compounds dissolved in liquids shorten the NMR relaxation times of liquid protons. (2) The quantity of certain other nuclear or electronic species can be measured directly by resonance measurements of those species.

Dissolved paramagnetic compounds will reduce the proton relaxation times of oils. Thus if two oils have the same viscosity, they will have different relaxation times if they have substantially different paramagnetic content. While many crude oils have negligible magnetic content, others have significant amounts of vanadium or nickel [Tissot and Welte, "Petroleum Formation and Occurrence", Springer-Verlag, 1978, Figure IV.1.20]. Because the relaxation effect is proportional to paramagnetic concentration, the proportions of two

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oils in a mixture can be monitored. Deliberate introduction of an oil-soluble paramagnetic substance into the oil base mud can considerably enhance this effect when the native crude is relatively free of paramagnetic material.

NMR-active nuclei can be monitored directly to determine contamination levels. OBM filtrates may differ from native oils by having substantially different concentrations of oxygen, sulfur, or nitrogen. Of these, nitrogen is the best NMR target because its NMR-active form, ^{14}N, has good NMR sensitivity and a reasonable natural abundance. Considerably greater sensitivity to contamination can be attained if trace elements are mixed with the drilling mud to mark the filtrate. For example, a fluorine-labeled organic compound can be detected directly by measuring the ^{19}F resonance; this would be a very sensitive probe of filtrate contamination.

Diffusion Coefficient: The diffusion coefficient is closely related to the viscosity; they are related by the approximate relation [J.C.M. Li, P. Chang, "Self Diffusion Coefficient and Viscosity in Liquids", J. Chem. Phys. 23, 518-520 (1955)]

$$D\eta = ckT\left(\frac{N}{V}\right)^{1/3} \tag{2}$$

where D is the diffusion coefficient, η is the viscosity, c is an empirical constant, k is Boltzmann's constant, T is the absolute temperature, and (N/V) is the number of molecules per unit volume. Thus in many cases, measurements of T_2 and diffusion coefficient are duplicative. However, T_2 is influenced by the presence of paramagnetics, whereas the diffusion coefficient is not. Thus diffusion measurements can be independently useful in determining contamination levels.

Proton Density: Crude oil's with API gravity greater than 20 have proton density equal to that of water [Vinegar et al, "Whole Core Analysis by 13C NMR", SPE Formation Evaluation 6, 183-189 (June 1991)]. On the other hand, some oil base mud filtrates can have proton densities below that of water. Where a proton density contrast exists, the proportions of mud filtrate and formation oil can be determined from NMR measurements of proton signal amplitude. Since the presence of solids or free gas in the flow stream also reduce the proton density sensed by the apparatus, the proton density technique may not be useful when those phases are present.

Molecular Conformation: In ordinary laboratory practice, NMR spectroscopy can be used to distinguish families of hydrocarbons from each other. For example, protons in ring compounds such as benzene and naphthalene, have slightly different resonant frequency than protons in alkanes. Thus OBM filtrates could be distinguished from formation oils if they have distinctive molecular conformations. Unlike the other techniques discussed so far, spectroscopy requires very good uniformity of the static magnetic field of the NMR

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apparatus: typically 1 part per million or better over the sample volume. This is routinely obtained with laboratory apparatus, and could be attained in the apparatus presented here.

3.1.2 Water Base Filtrate vs. Formation Water

NMR measurements can also help distinguish water base mud (WBM) filtrate from formation water. There will be little or no contrast in viscosity, diffusion coefficient, proton density, or molecular conformation. However, the trace element content can be considerably different. Water soluble paramagnetic ions (either natural of introduced) will have a strong relaxing effect, which can be used to monitor proportions of filtrate and connate water.

NMR is sensitive to sodium, so if filtrate and connate water have different salinity, sodium concentration provides a good measure of contamination. Moreover, measurement of the sodium concentration of formation water can be used to determine the water resistivity, Rw, an important parameter in resistivity log interpretation.

3.1.3 Oil vs. Water

Oil and water can be distinguished by many of the same techniques outlined above. Proton relaxation time differences may be based on viscosity, diffusion coefficient, paramagnetic relaxation agents, or other NMR-visible trace elements. The water phase will have a very narrow relaxation time distribution in contrast to crude oil, which often has a broad distribution.

Salt water has a large sodium NMR signal which will be absent in the oil phase. When oil and water are mixed in the flow line, they can frequently be quantified by relaxation time or other means. Then Rw can be determined by measuring the amplitude of the sodium NMR signal even in complex multiphase flows.

3.1.4 Gas

Gas is always a formation fluid; it is never a part of mud filtrates. Thus the quantity of gas evolved from the liquid during draw down is another measure of the relative proportions of mud filtrate and formation fluid.

NMR is sensitive to the density of hydrogen nuclei (protons). Oil and water often have similar proton density, whereas free gas has substantially lower proton density. Thus gas can be determined by an amplitude deficit relative to 100% liquid. Because gas has a long T_1 (typically greater than 4 sec at reservoir conditions), the NMR signal from gas is further reduced by incomplete polarization, enhancing contrast with liquid.

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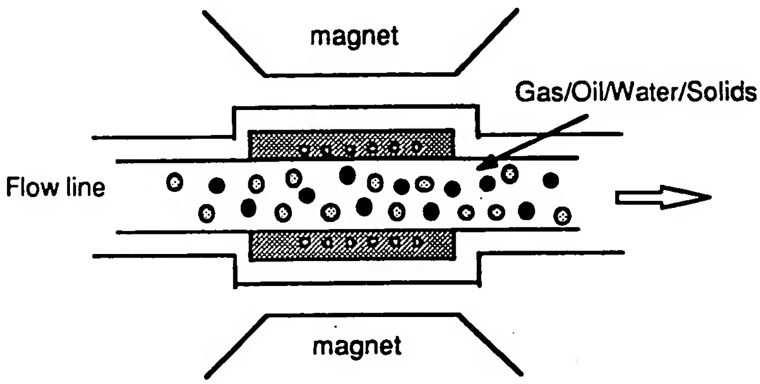
Gas may also be sensed directly and distinguished by techniques used in formation evaluation NMR measurements [Akkurt et al, "NMR Logging of Natural Gas Reservoirs", Log Analyst, Nov-Dec 1996, pg 33-42].

3.1.5 Apparatus and Technique

Apparatus: NMR apparatus can be built into the MDT flow line, allowing continuous monitoring of fluid entering the tool. A sketch is shown in Figure 1. The static magnetic field, B_O, is provided by an array of permanent magnets surrounding the metallic, but nonmagnetic, flow line. This field is transverse to the flow line axis, and substantially uniform in the volume occupied by fluid. One arrangement of permanent magnets is described by Halbach [K. Halbach, Nuc. Inst. Methods 169, 1-10 (1980); K. Halbach, Nuc. Inst. Methods 187, 109-117 (1981)].



Flow Line NMR

Figure 1

The oscillating magnetic field B_1 is produced by a solenoid potted into an insulating coil form, so that B_1 is perpendicular to B_O, as required for the NMR measurement. The coil form is placed on the inside wall of the flow line, where it effect on the strength of the tube is minimized. The metal tube surrounding reduces B_1 compared to its free space value, but also tends to make it more uniform in the fluid volume. To measure relaxation time, diffusion coefficient, or spin density (of hydrogen or other elements) neither B_O nor B_1 need be particularly uniform.

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Gradient coils can also be provided for the purpose of making pulsed field gradient measurements of diffusion coefficient and other quantities. If the static magnetic field is aligned with the z-axis, the most effective gradients are dB_z/dx, dB_z/dy, and dB_z/dz. A dB_z/dz gradient can be generated by a pair of saddle coils potted together with the coil which provides the B_1 field. Prescriptions for designing saddle coils that generate maximally uniform gradients can be found in the literature [R. Turner, "Gradient Coil Systems", Encyclopedia of Nuclear Magnetic Resonance, 1996].

The effect of flow velocity on measurements of relaxation times and spin density scale approximately as vT_1/L and vT_2/L where L is the length of the NMR apparatus, v is the flow velocity, and T_1 and T_2 are the NMR relaxation times of the fluid. The effect is similar to the speed effect of the NMR borehole logging tool. For a simplified discussion, see Fukuhara et al "Pulse Nuclear Magnetism Tool" SDR Report EMG-88-2 (1988). For a more complete discussion see Hurlimann, "Effects of Logging Speed on NMR Measurements", SDR Report EMG-006-96-21 (1996).

Technique: All standard NMR measurements can be made using the apparatus described. These include measurements of longitudinal and transverse relaxation times (T_1 and T_2) and, more generally, their distributions [R.L. Kleinberg, "NMR Methods for the Characterization of Porous Media", in Experimental Methods in the Physical Sciences: Methods of the Physics of Porous Media, P.-z. Wong, ed., Academic Press]; diffusion coefficient and other q-space measurements [Callaghan, "Principles of Nuclear Magnetic Resonance Microscopy", Clarendon Press, 1991]; flow velocity measurements [A. Caprihan and E. Fukushima, "Flow Measurements by NMR", Physics Reports, 198, 195-235 (1990); and chemical shift spectroscopy, if the B_0 field is sufficiently uniform.

Resonating nuclei other than ^1H is accomplished by changing the frequency of operation to match the Larmor frequency of the nucleus of interest.

3.2 Electron Spin Resonance

Electron spin resonance (ESR) is useful because of its great sensitivity to unpaired electron spins, even at very low spin density. Unpaired electrons are found in naturally occurring or artificially introduced magnetic transition metal ions such as iron, manganese, chromium, cobalt, vanadium and nickel. These last two are frequently found in crude oils, while chromium is found at high concentration in a number of water base mud filtrates. In general, mud filtrates and formation fluids will have different concentrations of transition metal ions, so ESR can be used to monitor the relative concentrations of filtrate and native fluids.

Unpaired electrons are also present in the free radicals of certain hydrocarbons, tertiary alkanes and alkyl benzenes, for example [Morrison and Boyd, Organic Chemistry,

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Allyn and Bacon, 1973]. The density of free radicals can be increased artificially by irradiating hydrocarbons with a low-level radioactive source located in the flow line upstream of the ESR cell. This can provide contrast between OBM filtrates and formation oils, which are likely to have differing amounts of compounds in which free radicals are stable.

ESR apparatus is similar to NMR apparatus. They can use the same magnet, or separate ones of similar design. Because ESR resonance frequencies are abut 700 times higher than proton NMR frequencies, a microwave resonator may be needed to provide the B_1 field.

3.3 Mixture Density

Density contrast can be used to distinguish mud filtrate from formation fluid, so it is desirable to measure density continuously as fluid is pumped through the MDT. Possible in-line density measurements use gamma ray scattering [K.-L. Giboni, "Concepts for an Improved Densitometer to Measure the Fluid Density in High Pressure Pipes", SDR Report, 1988] or X-ray scattering [K. Stephenson and J. Schweitzer, "Surface Metering of Three Phase Fluid Fractions and Mixture Density with X-ray Scattering and Transmission", SDR Patent Memo, 1993].

4. Pressure-Volume Cell Measurements

4.1 Bubble Point

Bubble point is determined in PVT laboratories by isothermally increasing the sample volume, V, (initially at reservoir pressure) and monitoring the pressure, P. Above the bubble point, $-\Delta P/\Delta V$ is large, but with the first appearance of free gas, $-\Delta P/\Delta V$ falls suddenly to a much lower value due to the large compressibility of the gas phase. The measurement can be made the same way inside the MDT.

The isothermal expansion can proceed in small steps, or continuously at a slow rate. The range of expansion should be 10% or more in steps of approximately 0.1%. Precision of the volume measurement is more important than constancy of the step size. The associated pressure measurement should have an absolute accuracy of better than 1 psi (7 kPa).

4.2 Dew Point

The dew point is the most important thermodynamic parameter associated with gas condensate reservoirs. There is no strong signature in the P-V characteristic at the dew point, because the first appearance of liquid does not substantially change the compressibility of the mixture. Thus it is necessary to directly sense the liquid phase. To

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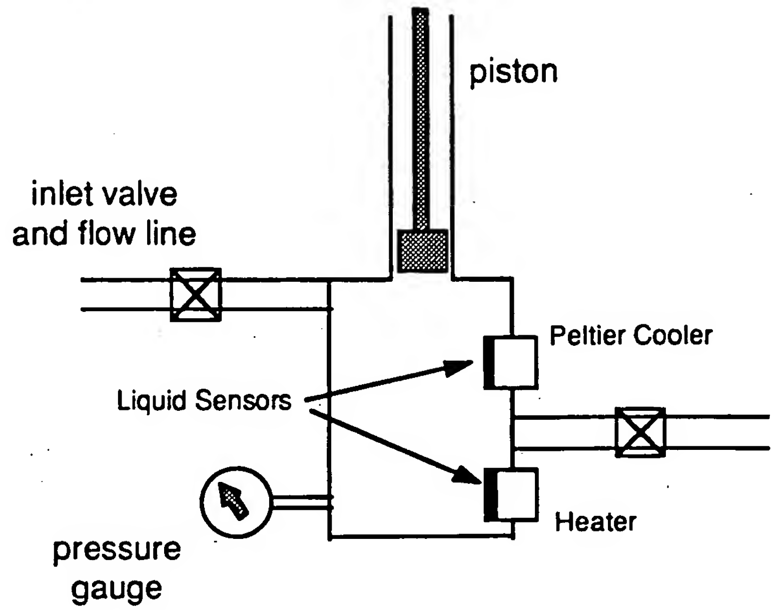
do this, the first condensation must be on a moisture sensor, such as the one described by H. Ziegler and K. Rolf, "Quartz Sensor for Automatic Dew-Point Hygrometry", Sensors and Actuators, 11, 37-44 (1987).



Dew Point Cell

Figure 2

Dew point sensors are normally integrated with coolers so that first condensation occurs on the sensor. However, mixtures of hydrocarbons found in reservoirs can have unusual phase diagrams: first condensation can occur at the hottest point accessible to the mixture [Amyx, Bass, Whiting, "Petroleum Reservoir Engineering", McGraw-Hill, 1960, pg 220-229]. Thus moisture sensors must be mounted on both a heater and a cooler in order to ensure that the dew point will be accurately measured under any circumstances. A schematic of a bubble point/dew point cell is shown in Figure 2. The Peltier cooler and heater can be integrated into a single device.

4.3 Liquid Density

It is useful to monitor physical properties of the liquid as a function of pressure during a bubble point decompression procedure. The pressure dependence of liquid density is of particular interest to reservoir engineers. It is usually expressed in terms of formation volume factor, which is inversely proportional to density.

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To be useful, a density sensor must have a resolution of 0.01 g/cm^3, which corresponds to be 2 units of API gravity. It must work in the high pressure, high temperature environment of the tool, and it must work independent of tool orientation.

Density within the PV cell can be measured with a buoyancy device, see Figure 3. A sphere with a net density $\rho_s \sim 1$ g/cm^3 is mounted at the end of a leaf spring. In liquids with density different than ρ_s the buoyant force on the sphere will be balanced by the restoring force of the leaf spring. The displacement can be very accurately measured by a capacitive position sensor [R.V. Jones and J.C.S. Richards, "The Design and Some Applications of Sensitive Capacitive Micrometers", Journal of Physics E 6, 589-600 (1973)]. The apparatus is calibrated using liquids of known density.

Density Measurement

Buoyancy Sensor in Passive Gimbal

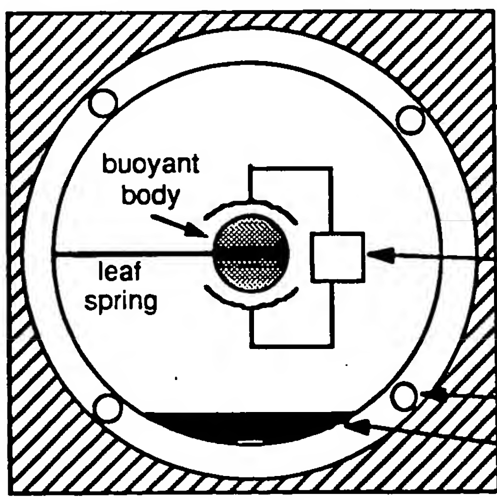

Figure 3

Because the buoyant force is gravitational in nature, the motion of the sphere must be along the plumb line. This is ensured by gimballing the sensor. The gimbal may be passive or driven; both techniques are well known. The passive gimbal moves freely and has a weighted keel at the bottom to ensure a constant orientation with respect to local gravity. The driven gimbal utilizes a feedback system in which a tiltmeter acts as a sense element and a two-axis motorized drive is used to bring the tiltmeter to null.

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4.4 Viscosity

NMR can be used to measure liquid viscosity during depressurization. Liquid viscosity changes substantially upon evolution of gas; thus this measurement is useful in predicting the producibility of the formation over time. The apparatus is similar to the flow line NMR apparatus discussed above.

4.5 Gas Composition

Methane is usually the main constituent of reservoir gas, but ethane, propane, butane, carbon dioxide, nitrogen, and water vapor can also be present in substantial volumes. While a complete downhole characterization of composition may not be possible, partial analysis, combined with optical or other techniques, is useful.

Gas composition can be estimated by measuring its density at one or more pressures. For a pure gas at low pressure the density ρ and pressure P are related by the ideal gas law

$$\frac{\rho}{P} = \frac{M}{RT} \tag{3}$$

where M (grams/mole) is the molecular weight of the gas, R = 0.08205 liter-atm/(mole·K) is the gas constant, and T (degrees Kelvin) is the absolute temperature. Thus, under ideal conditions, the ratio ρ/P measured at a known temperature distinguishes gases of different molecular weights.

The ideal gas law only holds at relatively low pressure, much less than typical reservoir temperature. At high pressure it must be modified

$$\frac{\rho}{P} = \frac{M}{ZRT} \tag{4}$$

where Z is the compressibility, which is itself a function of pressure and temperature. However, the function ρ(P) is characteristic of a pure gas, and serves to identify it. For a mixture of gases at high pressure, the situation is more complicated, but not intractable. Properties of gas mixtures are described in the petroleum engineering literature [Amyx, Bass, Whiting, "Petroleum Reservoir Engineering", McGraw-Hill, 1960, chap. 4].

Gas density is conveniently and accurately measured with a vibrating quartz crystal similar to those used in wrist watches [R.W. Ward and E.P. EerNisse, "A Quartz Fluid Density Sensor Pressure Transducer", 40th Annual Frequency Control Symposium (1986)

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pg 211-215]. The sensing crystal must be protected ~~by~~ from liquid, so this measurement must be made in a separate chamber to which only gas can be admitted. RLK 6 Aug 97

4.6 Bubble Control

The pressure dependence of liquid (as opposed to gas-liquid mixture) properties are of particular interest. The presence of bubbles can corrupt such measurements. Thus it is useful to make sure that bubbles form well away from any ancillary measurement apparatus. Provision of a heater is not sufficient to localize bubble formation, because complex hydrocarbon liquids can have unusual phase diagrams [Amyx, Bass, Whiting, "Petroleum Reservoir Engineering", McGraw-Hill, 1960, chap. 4]. Thus both a hot spot and a cold spot must be provided within the bubble point cell to ensure bubble localization. A Peltier cooler provides both a hot point and a cold point [J. Bass, "Thermoelectricity", in McGraw Hill Encyclopedia of Science and Technology]. The requirements are the same as that for the dew point cell discussed above.

Cavitation is another means of bubble localization. A source of sound will encourage the formation of bubbles in its vicinity. It is generally thought that cavitation is not effective above a hundred psi of liquid pressure. However, near the bubble point, bubbles will form readily no matter what the pressure.

Once bubbles form, they must be prevented from migrating to the ancillary sensors. Shrouds, which do not interfere with pressure continuity but which impede the migration of bubbles, can be employed within the PV cell.

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EXHIBIT B

Patents

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MEMORANDUM

TO: PATENTS August 18, 1997

FROM: Michael Oristaglio

SUBJECT: Patent Memo

Attached is an original Patent Memorandum entitled, "Downhole PVT Lab for MDT" by R.L. Kleinberg dated 5 August, 1997.

Enclosure

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60.1324

SCHLUMBERGER-DOLL RESEARCH
DIVISION OF SCHLUMBERGER TECHNOLOGY CORPORATION

PATENT MEMORANDUM

Inventor: **R.L. Kleinberg** Date: 29 August 1997

Title of Invention: **Flow Line NMR Measurements for MDT**

1. Introduction

Quantitative fluid analysis in the MDT prior to, or instead of, conveyance of a sample to the surface, will improve measurement accuracy and efficiency.

Several techniques are currently used in the MDT to provide a partial analysis:

Resistivity: Indicates the presence of water. The measurement uses the low frequency electrode technique. Unless there is a continuous conducting path between the electrodes, there is no sensitivity to the presence of water. Even with a conducting path, the method is unable to separate the effects of water volume, salinity, and flow geometry. The measurement is simple and often useful, but inherently nonquantitative.

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Optical Fluid Analyzer: In the absence of gas, OFA gives quantitative oil and water volumes. In favorable cases, oil base mud filtrate can be distinguished from native oil. Water base mud filtrate cannot be distinguished from native water. The OFA detects gas, but in the presence of gas or particulates, the ability to quantitatively measure volumes is lost.

Flow Line Pressure and Temperature: Provide no information on fluid properties.

Nuclear magnetic resonance (NMR) is a powerful fluid characterization technique. The volumes of individual components of fluid mixtures, and some physical properties of each component, can be measured. The method is inherently noninvasive and noncontacting. Since NMR measurements are volumetric averages, they are insensitive to flow regime, bubble size, and identity of the continuous phase.

The flow line of the MDT is a natural environment in which to make NMR measurements [R.L. Kleinberg, "Downhole PVT Lab for MDT", 5 August 1997]. The volumetric fractions of gas, oil, and water; the salinity of water; and the viscosity of oil, are usefully measured in the MDT. This report describes how and under what conditions they can be measured by NMR.

2. Static Measurements

A full range of quantitative NMR measurements can be made at the completion of pumpout, while formation fluid is at rest in the flow line.

2.1 Volume Fractions

2.1.1 Basic Equation

The calibrated NMR signal from a mixture of gas, oil, and water is

$$S = V_{water} \times HI_{water} \times [1-\exp(-W/T_{1water})] + V_{oil} \times HI_{oil} \times [1-\exp(-W/T_{1oil})] + V_{gas} \times HI_{gas} \times [1-\exp(-W/T_{1gas})] \quad (1)$$

V_{water}, V_{oil} and V_{gas} are proportional to the volumes of each fluid. HI (hydrogen index) is the proton density for each fluid, normalized to the proton density of water at 20°C and 1 atmosphere pressure. The last factor on each line is a correction to account for insufficient polarization time W.

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Water, oil, and gas signals can be separated by methods described below. To obtain the fluid volumes from resolved NMR signals, the hydrogen index must be determined. The situation is different for each fluid. For charts of hydrogen index, see R.L. Kleinberg, H.J. Vinegar, Log Analyst, Nov.-Dec. 1996, pg. 20.

Water: HI_{water} is defined to be unity at room temperature and pressure; the effects of elevated temperature and pressure are tabulated [Amyx, Bass and Whiting, Petroleum Reservoir Engineering, 1960, pg 458]. A larger correction to HI_{water} is due to salinity. Thus the salt content of the water must be known to obtain an accurate volume. The solubility of natural gas in water is low, and therefore does not have a significant effect on hydrogen index.

Oil: For oil at room temperature and pressure, without dissolved gas, hydrogen index is unity for API gravity greater than 20, which is the range of interest for the MDT. HI_{oil} will track density as a function of temperature and pressure. There is no generally accepted correlation between HI_{oil} and dissolved gas content [Kimminau, "The Hydrocarbon Correction" SWS-IE Memo, 13 April 1984].

Gas: HI_{gas} is in the range of 0-0.6 for oilfield conditions, so the gas signal is not negligible. HI_{gas} depends on temperature and pressure, which are measured in the MDT, and chemical composition, which is not. Carbon dioxide has no proton NMR signal, and thus may be obtained by difference when the volumes of water, oil, and natural gas are measured directly.

2.1.2 Relaxation Time Analysis

2.1.2.1 Water and Oil in the Absence of Gas:

Water in the MDT flow line at downhole temperature and pressure will have relaxation times of several seconds; the decay is expected to be described by a single exponential. The magnetization decay of crude oils is multiexponential, but when the downhole viscosity of oil is greater than a few centipoise, water and oil NMR signals will have distinctly different relaxation times [R.L. Kleinberg, H.J. Vinegar, Log Analyst, Nov.-Dec. 1996, pg. 20.]. This enables oil and water signals to be separated using a T_2 distribution, as is familiar from NMR formation evaluation. If the water and oil signals are well resolved in the T_2 distribution, in the absence of free gas, the areas under each peak are equal to

$$V_{water} \times HI_{water} \times [1-\exp(-W/T_{1water})] \tag{2a}$$

and

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$$V_{oil} \times HI_{oil} \times [1-\exp(-W/T_{1oil})]$$

(2b)

respectively. $T_1 = T_2$ for liquids in the flow line apparatus, so if T_2 is measured by the CPMG pulse sequence, the polarization correction can be accurately computed.

2.1.2.2 Gas Measurements

The relaxation time of gas is a function only of its temperature and pressure, which are measured. For free gas in the absence of magnetic field gradients, $T_1 = T_2$, in the range of several seconds, and the decay is single exponential [Straley, 1997 SPWLA]. Thus the decay time of free gas can coincide with water and light oil. Gas is distinguished from liquids by its diffusion coefficient. Either of two methods may be used:

Gas Diffusion-Relaxation Method 1:

(1) The transverse magnetization decay is measured by CPMG in the usual manner, and the T_2 distribution is determined. Gas relaxes with relaxation time $T_{2,bulk}$.

(2) The transverse magnetization decay is measured by CPMG in the presence of a uniform, steady magnetic field gradient supplied by gradient coils [Kleinberg, "Downhole PVT Lab for MDT", sec. 2.1.5]. The relaxation rate of gas is then

$$\frac{1}{T_2} = \frac{1}{T_{2,bulk}} + \frac{(\gamma G T_E)^2 D}{12}$$

(3)

where γ is the gyromagnetic ratio, G is the applied gradient, T_E is the CPMG echo spacing, and D is the diffusion coefficient. Since $T_{2,bulk}$ and all these parameters are known, the two measurements can be readily analyzed for the gas signal.

Gas Diffusion-Relaxation Method 2:

A pulsed field gradient technique can be used, analogous to that described by Kleinberg, Latour and Sezginer [SDR Docket 60.1110, 1995].

2.1.3 Chemical Shift Analysis

Proton NMR chemical shift can also be used to distinguish fluids [Vinegar US 5,306,640 (1994)]. Gas, light oil, and water have distinct chemical shifts [Dyer, Applications of Absorption Spectroscopy of Organic Compounds (1965)]

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	TMS	CH_4	H_3C-C	$-CH_2-$	H_2O
Shift (ppm)	10	9.77	9.1	8.7	4.7

Note that the chemical shift of methane depends on pressure [Trappeniers and Oldenziel, Physica 82A, 581 (1976)], and whether it is in the gas phase or in solution [Rummens and Mourits, Canadian Journal of Chemistry 55, 3021 (1977)].

Fluids are distinguished when the B_0 measurement field is homogeneous to better than 1 part per million. Homogeneity at this level can be achieved by techniques previously described [Kleinberg, "Downhole PVT Lab for MDT", sec. 3.1.5]. The area under the spectral lines is proportional to fluid volumes as described by Eqn (1). Chemical shift spectroscopy is particularly useful when oil and water have similar relaxation times.

2.1.4 Carbon NMR

Carbon may be found in some formation waters, as carbonate or bicarbonate ion, but it predominates in oil and gas. Thus in many cases, a measurement of carbon amplitude gives a direct measurement of hydrocarbon quantity. The NMR-active isotope of carbon is ^{13}C, which has a natural abundance of about 1%. At natural abundance, its NMR visibility is rather low, 1.75×10^{-4} relative to ^1H, see Appendix. Relaxation times tend to be long, making signal accumulation slow. Thus apparatus with good signal to noise ratio is helpful in making ^{13}C measurements. Cross-polarization techniques increase signal to noise ratio [Gerstein and Dybowski, Transient Techniques in NMR of Solids, 1985].

2.2 Oil Viscosity

Oil viscosity can be determined if the oil signal is resolved from other fluid signals by either relaxation analysis (section 2.1.2) or chemical shift analysis (2.1.3).

When relaxation analysis is used, T_2 is measured directly. As stated above, crude oils have broad distributions of relaxation times. However, it has been found that oils with low viscosity relax more slowly than those with higher viscosity [C.E. Morriss, R. Freedman, C. Straley, M. Johnston, H.J. Vinegar, P.N. Tutunjian, in Transactions of the SPWLA 35th Annual Logging Symposium, 1994; Log Analyst, March-April 1997, pg 44.]. A single relaxation time parameter which captures the viscosity dependence is the logarithmic mean T_2:

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$$T_{2LM} = \exp\left[\frac{\sum_i m_i \log_e(T_{2i})}{\sum_i m_i}\right] \quad (4)$$

It has been found that over the range 1 cp to 300 cp, and in the absence of an applied magnetic field gradient, T_{2LM} (in seconds) is related to viscosity η (in centipoise)

$$T_{2LM} = \frac{1.2}{\eta^{0.9}} \quad (5)$$

When chemical shift analysis is used, the longitudinal relaxation time, T_1, of each spectral line can be determined by standard methods [Vinegar US 5,306,640 (1994)]. Then viscosity can be found from Eqn (5) using $T_1 = T_2$ for crude oils in the absence of magnetic field gradients [Straley and Vinegar, unpublished].

2.3 Water Phase Salinity

Determination of oil saturation from deep resistivity measurements requires knowledge of the water resistivity, R_w. The present MDT resistivity measurement is a low-frequency current injection technique, which is unable to measure R_w in the presence of hydrocarbon. It is possible to estimate R_w by measuring the concentration of current-carrying ions. Measuring the individual concentrations of dissolved ions in the water phase is also very useful in interpreting flow line nuclear measurements of density and Pe. The common ions in reservoir waters are [Petroleum Engineering Handbook, Chapter 24]:

cations: Ca, Mg, Na

anions: CO_3, HCO_3, SO_4, Cl

Among the cations, sodium often dominates, but there can be significant quantities of calcium and magnesium in some areas. Chlorine usually dominates anion concentration, although there are some areas where carbonate, bicarbonate, or sulfate are important.

Solubility limits the combinations of ions that can be present simultaneously [CRC Handbook of Chemistry and Physics, pg B-73 et seq.]. Note that solubilities can be modified by acidity, and depend on temperature.

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Relatively soluble combinations:

Cation	Anion	Solubility (g/l) (hot water)
Na	Cl	391
Na	CO_3	455
Na	SO_4	425
Ca	Cl	1590
Mg	Cl	727
Mg	SO_4	738

Relatively insoluble combinations:

Cation	Anion	Solubility (g/l) (hot water)
Ca	CO_3	0.019
Ca	SO_4	0.162
Mg	CO_3	0.106

Thus high concentrations of calcium are incompatible with high levels of carbonate or sulfate, while high levels of magnesium are incompatible with high levels of carbonate. The magnesium sulfates (epsomite, kieserite) are not particularly common minerals, and magnesium and sulfate ion are rarely seen together at high concentrations [Petroleum Engineering Handbook, Chapter 24]. Thus measuring sodium and chloride, and applying the condition of charge neutrality, constrains the composition of oilfield waters. Thus we can identify "sodium waters"

$$[Na^+]-[Cl^-] = 2\,([CO_3^{--}]+[SO_4^{--}]) \quad \text{for } [Na^+]-[Cl^-]>0 \tag{6}$$

and "chloride waters"

$$[Cl^-]-[Na^+] = 2\,([Ca^{++}]+[Mg^{++}]) \quad \text{for } [Cl^-]-[Na^+]>0 \tag{7}$$

Thus total salinity (maximum of $[Na^+]$ and $[Cl^-]$) and some estimate of ion identity can be obtained, and used to estimate water conductivity, density, and Pe.

By changing the operating frequency of the NMR apparatus, the quantities of various isotopes can be determined. A table of NMR properties of commonly occurring elements in oilfield fluids may be found in the Appendix. The best isotopes for NMR measurements are ^1H, ^{23}Na and ^{35}Cl. The NMR amplitude of the sodium or chlorine resonance will give the volume of water multiplied by the concentration of the ion.

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2.4 Oil Composition

One of the primary products of conventional PVT analysis is oil composition. There are two methods by which NMR can provide at least a partial composition analysis: spectroscopy and relaxation time analysis.

2.4.1 Spectroscopy

The NMR chemical shift depends on the molecular environment of a spin. Thus chemical conformation can be determined; this is one of the oldest and most widespread uses of nuclear magnetic resonance. Crude oils are complex mixtures of hydrocarbons, and NMR spectroscopy is used to identify characteristic bands. For example, aliphatic protons appear in one frequency band, while aromatic protons appear at another; both are distinguishable from water [Vinegar US 5,306,640 (1994)]. Chemical shift spectroscopy can performed using either ^{1}H or ^{13}C [Petrakis and Edelheit, Applied Spectroscopy Reviews 15, 195 (1979); Botto, "Fossil Fuels", Encyclopedia of Nuclear Magnetic Resonance (1996)].

2.4.2 Relaxation Time Analysis

The relaxation time depends on correlation times due to molecular motion [Bloembergen, Purcell and Pound, Physical Review 73, 679 (1948)]. Protons in large molecules tend to move slower, and hence relax faster, than those in ~~slow~~ molecules. small RLK 5Sept97
Crude oils are mixtures of pure hydrocarbons, and have broad distributions of relaxation times [C.E. Morriss, R. Freedman, C. Straley, M. Johnston, H.J. Vinegar, P.N. Tutunjian, in Transactions of the SPWLA 35th Annual Logging Symposium, 1994; Log Analyst, March-April 1997, pg 44]. Thus there may be composition information in relaxation time distributions.

3. Dynamic Measurements

During pumpout, fluid may be moving at a high rate of speed through the flow line NMR apparatus. This limits polarization time and signal acquisition time, so some types of quantitative measurements may not be possible. However, there are a number of methods by which contamination can be monitored qualitatively.

3.1 Speed Effects

The rate that fluid moves through the tool depends on the permeability of the earth formation, the viscosity of the fluid, and the rate at which fluid can be pumped through the tool and into the borehole. The flow control module allows flows in the range 1 - 500 cm^3/s, while the pumpout module operates at speeds up to about 40 cm^3/s.

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["Schlumberger Wireline Formation Testing and Sampling" (1996) pg. 4-29, 4-40]. The flow line has an inside diameter of 0.5 cm, so 500 cm^3/s corresponds to a flow speed of 25.5 m/s while 40 cm^3/s corresponds to a flow speed of 2 m/s. The effect of flow is similar to the speed effect of the CMR [Hurlimann, "Effects of Logging Speed on NMR Measurements", SDR Research Note, 1996].

Quantitative NMR measurements require that the spins be fully polarized by the static magnetic field prior to data acquisition. This requires that the spins be exposed to Bo for three to five times as long as the longitudinal relaxation time T_1. For water or light oils at high temperature, T_1 can be several seconds; thus wait times of 10 seconds or more will be required. Since the NMR apparatus is expected to be about 0.3 m long, even moderate flow speeds prevent quantitative measurements from being made during pumpout. However, limited measurements to detect contamination can be made during pumpout. When contamination is at a sufficiently low level, pumping is stopped and the full range of quantitative measurements are made.

3.2 Hydrogen Amplitude

Hydrogen NMR amplitude is controlled by hydrogen index and the effect of incomplete polarization, see Eqn (1).

Medium-to-Heavy Oil/Water: The more viscous the oil, the more completely it will be polarized, because viscous oils relax quickly and flow slowly (at least in some flow regimes). In contrast, the viscosity of produced water is less than 1 centipoise. If the flow speed of water is measured by other means, the effect of flow on water proton amplitude is determined by apparatus geometry and pulse sequence parameters. Thus the amounts of water and medium-to-heavy oil can be determined from the proton signal amplitude. Note however, that the presence of gas will mimic incompletely polarized water, so this technique has limited validity in the presence of gas.

Medium-to-Heavy Oil/Oil Base Mud Filtrate: This situation is rather similar to the medium-to-heavy oil/water case just discussed. Oil base mud filtrates have T_1's in the range of several hundred milliseconds, and thus will not be completely polarized in a rapidly moving stream. As the ratio of heavier formation oil increases, signal amplitude increases.

Light Oil and Gas/Oil Base Mud Filtrate: This is the most important contamination detection problem, and the one the OFA has the most trouble with. In this case, native oil has a longer relaxation time than OBM filtrate. Thus as the proportion of native fluid increases, the proton signal amplitude will decrease. The presence of free gas associated with native oil accentuates the contrast. Signal level will stabilize at a low level when OBM contamination has been eliminated.

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Light Oil and Gas/Water Base Mud Filtrate: This situation is similar to the OBM situation, but contrast is somewhat reduced because WBM filtrates often have relaxation times intermediate between OBM filtrates and native oils. However, the method will still work, especially in the presence of formation gas, which depresses the total signal as water contamination diminishes.

Effect of Paramagnetic Ions in the Filtrate: The use of chromium lignosulfonate muds, or manganese tracers used for formation evaluation [Horkowitz et al, 1995 SPWLA Paper Q], add paramagnetic ions to the filtrate. These ions reduce the filtrate relaxation time. Thus they increase contrast with light oils and gas, and decrease contrast with medium to heavy oils. Paramagnetic ion can also be introduced in the flow line. $2x10^{18}$ ions/cm^3 of Fe^{3+} will reduce water T_1 to 30 msec [Andrew, Nuclear Magnetic Resonance (1955)]. This is equivalent to 54 grams $FeCl_3$ per 100 liters of water. For flow line doping to work, the water must be the continuous phase, and come into contact with the source of ions.

3.3 Hydrogen Spectroscopy

Proton spectra can be obtained very efficiently by conventional pulse NMR techniques. Water and oil are readily distinguishable in the spectra, as described in section 2.1.3. Incomplete polarization and hydrogen index effects reduce the amplitudes of individual spectral lines. The effects are the same as those described in section 3.2. Monitoring the spectrum during pumpout provides fluid-selective information. For example, T_1 changes in the oil phase can be monitored independent of the signal from water.

If the chemical shift is different for oil base mud filtrate and native oil, monitoring the location of the peak of the oil spectral line can be used to monitor contamination.

3.4 Sodium and Potassium NMR

Sodium longitudinal relaxation time is 47 ms at 2 MHz and room conditions [Farooqui et al, "Nuclear Magnetic Resonance of 23Na", EMG-006 report, 22 October 1996]. Thus the amplitude of the sodium resonance can be measured at least semi-quantitatively during flow. This is a good way of monitoring water contamination of oil samples, even in the presence of gas. Secondarily, water base mud can be distinguished from formation water on the basis of sodium content.

Potassium is particularly interesting because of its large concentration in KCl muds. Monitoring potassium NMR amplitude is a direct measure of contamination when KCl mud has been used. The longitudinal relaxation time of potassium in aqueous solution is 38 msec [Decter, Progress in Inorganic Chemistry 29, 285 (1982)] so speed effect is minor.

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Appendix: N[redacted]MR Properties of Elements Common in Oilfield Fluids

Isotope	~~Frequency~~ Frequency(^{1}H)	Natural Abundance	NMR Sensitivity(1)	Net Sensitivity(2)
^{1}H	1	1.00	1	1
^{13}C	0.251	0.011	1.59×10^{-2}	1.75×10^{-4}
^{17}O	0.136	3.7×10^{-4}	2.91×10^{-2}	1.08×10^{-5}
^{23}Na	0.264	1.00	9.25×10^{-2}	9.25×10^{-2}
^{25}Mg	0.061	0.101	2.67×10^{-3}	2.70×10^{-4}
^{33}S	0.076	0.0076	2.26×10^{-3}	1.72×10^{-5}
^{35}Cl	0.098	0.755	4.70×10^{-3}	3.55×10^{-3}
^{37}Cl	0.082	0.245	2.71×10^{-3}	6.63×10^{-4}
^{39}K	0.047	0.931	5.08×10^{-4}	4.74×10^{-4}

(1)At 100% a[redacted]bundance, ^{1}H = 1
(2)At natural [redacted]abundance, ^{1}H = 1

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8-29-1997 SDR Ridgefield
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EXHIBIT D

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MEMORANDUM

TO: PATENTS September 15, 1997

FROM: Michael Oristaglio

SUBJECT: Patent Memo

Attached is an original Patent Memorandum entitled, "Flow Line NMR Measurements for MDT" by R.L. Kleinberg dated 29 August, 1997.

Enclosure

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Schlumberger

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Via First Class

October 21, 1997

Mark Levy, Esq.
Salzman & Levy
Press Building Suite 606
19 Chenango Street
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Re: New Patent Application of R. L. Kleinberg
for "Downhole PVT Lab for MDT"
(Our File 60.1323)

New Patent Application of R. L. Kleinberg
for "Flow Line NMR Measurements for MDT"
(Our File 60.1324)

Dear Mark:

I enclose a copy of the above-identified Patent Memos, for which we would like you to prepare one or more patent applications.

I expect to send you two more related patent memos in about a week.

All of these inventions relate to improvements to the MDT (Modular Formation Dynamics Tester) of which you will find a brief description on page 70 of the Schlumberger Wireline Services Catalog. We also enclose additional, more technical, documentation on the MDT.

You will be able to discuss these four inventions with Bob Kleinberg during your next visit.

Sincerely yours,

Keith Smith

Keith Smith

KS:rs
enclosure

cc: R. L. Kleinberg

EXHIBIT F

ROBERT S. SALZMAN
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SDR PATENTS
JAN - 8 1998
FILE 60.1323 cc: R. Kleinberg - OKay 1-8-98
DOCK'D

January 6, 1998

Mr. Keith Smith
Patent Manager
SCHLUMBERGER-DOLL RESEARCH
Old Quarry Road
Ridgefield, CT 06877-4108

Re: Docket No. S-60-1323

Dear Keith:

Attached for Bob Kleinberg's review is a draft of the above-identified patent application. PLEASE HAVE HIM TAKE THE TIME TO REVIEW THE ENTIRE APPLICATION INCLUDING ALL CLAIMS AND DRAWINGS FOR COMPLETENESS AND TECHNICAL ACCURACY. Have him pay particular attention to adding information, if necessary, which is adequate to permit one skilled in the art to practice the invention without undue experimentation. As of the date we file the application, it should include a description of the best mode of which he is aware, for carrying out his invention. Therefore, please let us know IMMEDIATELY if he improves or changes the invention beyond the present description. After his approval, the application will be filed in the U.S. Patent and Trademark Office (PTO).

THE LAW IMPOSES A DUTY OF CANDOR AND GOOD FAITH ON ALL PERSONS INVOLVED IN PROCEEDINGS WITH THE PTO. This duty requires that he does not misrepresent test results nor misrepresent what the prior art contains. This duty also requires him to disclose all material information known to him which has a bearing on the patentability of the invention claimed in the application.

MATERIAL INFORMATION includes patents, printed publications, information on possible prior public uses, sales, offers to sell, prior invention by another and inventorship conflicts. In short, it is any information, the disclosure of which a reasonable examiner would be likely to consider important in deciding whether to allow the application to issue as a

patent. It is not limited to information which would render the claims unpatentable.

IT IS ESSENTIAL THAT ALL ITEMS NOTED ABOVE, AS WELL AS ANY OTHER INFORMATION YOU BELIEVE MAY HAVE A BEARING ON THE CLAIMED INVENTION, BE BROUGHT TO OUR ATTENTION PROMPTLY, AT ANY TIME DURING PROSECUTION. If he has any doubt or question about whether any particular information is material, please err on the safe side and bring it to our attention. In this manner he can satisfy his duty of disclosure and we can ensure that all material information of which we are aware is disclosed to the PTO.

THEIR DUTY ALSO EXTENDS TO MATERIAL INFORMATION WHICH COMES TO YOUR ATTENTION IN THE FUTURE. Should he later acquire any material information while the application is still pending, kindly disclose it to us promptly.

Sincerely,

Mark Levy

ML/kw
Enclosure

EXHIBIT G

Schlumberger

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KEITH SMITH
Patent Manager

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Courier

March 20, 1998

Mark Levy, Esq.
Salzman & Levy
Press Building Suite 606
19 Chenango Street
Binghamton, NY 13901

Re: New Patent Applications of Robert L. Kleinberg
for "Downhole PVT Lab for MDT " (Our File 60.1323)
and "Flow Line NMR Measurements for MDT" (Our File 60.1324)

Dear Mark:

Thank you for your letter of January 6, 1998, enclosing a draft patent application, which we believe was intended to include both the above patent memorandums.

We feel this draft needs considerable re-work. Bob Kleinberg has poduced two new documents, which are included herewith. These documents do not correspond exactly to the way these inventions were originally presented, but for the sake of continuity, we have somewhat arbitrarily maintained the same file numbers, using the best correspondence (in spite of the confusing titles).

Please review these documents prior to our meeting here at Ridgefield on Tuesday, March 31, 1998. I would also like you to think about drawings for these two cases.

Very truly yours,

Keith Smith

Keith Smith

/rs
enclosure

cc: R. Kleinberg